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Calorimetric study of the heat effects induced by the fixation of hydrogen sulphide on the surface of modified activated carbon fibres

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ABSTRACT

In order to improve their efficiency for the removal of H₂S contained in polluted effluents, activated carbon fibres are impregnated by KOH aqueous solutions. In presence of water vapour, H₂S is not simply physically adsorbed on the surface of the treated cloths but several reactions can occur. The fixation mechanism proposed has been validated and completed through the calorimetric study of the heat effects induced by the reactions that occur when the treated fibres are in contact with a gas mixture of H₂O and H₂S.

KEY-WORDS

Calorimetry; activated carbon fibres; hydrogen sulphide

INTRODUCTION

Activated carbon fibres, as activated carbons, are known to be very good adsorbents. They are highly porous: their specific surface areas often exceed a BET value (conventional method) of 1200 m².g⁻¹. Many chemical groups such as red-ox and acid-base couples resulting from the manufacturing process are distributed on their surface.

Activated carbons come from the activation of any carbonaceous material. The activation treatment consists of two distinct steps: the carbonisation followed by the activation itself. During carbonisation, volatile organic components are eliminated, the carbons rearrange themselves into graphitic sheets laid out in a random way ^[1]. During activation, an oxidising agent attacks the carbons located at the edges of the graphitic sheets, this step is responsible for the creation and development of the porosity and surface groups ^[2-3].

The application the fibres studied are devoted to is the filtering at room temperature (25°C) of gas mixtures containing very small amounts of hydrogen sulphide (few vpm). Under these conditions, hydrogen sulphide is weakly adsorbed by the activated fibres. An interesting route to improve these sorption capacities consists in impregnating the activated fibres ^[4] with a basic solution in order to create basic functions which will favour reactions between H₂S and the impregnate. The treatment chosen consists in an impregnation of the activated fibres by an aqueous solution of potassium hydroxide ^[5, 6].

The impregnation treatment greatly increases the H₂S fixation capacities of the activated carbon fibres. On the impregnated cloths, H₂S molecules are not simply adsorbed but several reactions occur. The fixation mechanism has been clarified using characterisation techniques and measurements of the fibres capacities to retain H₂S. All the reactions involved in the mechanism proposed present heat effects which can be detected and quantified by calorimetry. Thus, the study of the heat effects by this technique is a way to validate the H₂S fixation mechanism and eventually to evidence unsuspected reactions.

MATERIAL AND METHODS

The activated carbons studied are commercial carbon fibres coming from the activation of rayon fibres. Their specific surface areas reach 1400 m².g⁻¹ and they are mainly microporous. In the laboratory these fibres are impregnated with potassium hydroxide aqueous solutions.

The impregnation protocol consists in immersing for 20 minutes the cloths into an aqueous solutions of potassium hydroxide. The cloths are then taken out of the solution and dried under air during 2 hours at 100°C. The treatment ends with a thermal treatment performed at 25°C under deep vacuum. The KOH molecules deposited on the fibres surface after immersion in the impregnation solution are carbonated onto KHCO_3 by CO_2 of air and then decomposed into K_2CO_3 during the thermal treatment^[7].

The non treated fibres will be called virgin fibres, the treated ones KOH C_{KOH} , where C_{KOH} is the concentration of the impregnated solution in g.L^{-1} (e.g. : KOH 10).

The apparatus for the measurement of the H_2S fixation capacities of the virgin and the impregnated fibres is illustrated on figure 1. A sample of cloth is held in a reactor surrounded by a double walled vessel. The working temperature is controlled by the water circulating between the two walls. The reactor is crossed by a gas mixture containing nitrogen, water vapour and hydrogen sulphide^[8]. Preliminary experiments have highlighted that the presence of water vapour in the gas mixture strongly enhances the H_2S fixation capacities of the fibres. The working temperature is fixed at 25°C. The gas flow Φ is 30 L.h^{-1} , the volumic fraction θ of H_2S is fixed to 50 vpm and the relative humidity to 30% at 25°C. A photo ionisation gas detector (PID) records the volumic fraction of H_2S coming out of the reactor as a function of time. From the data collected, breakthrough curves can be plotted. The capacities of H_2S fixation (expressed as the amount of H_2S fixed per unit of mass of fibres: mol.g^{-1}) of the cloths are calculated by integration of these curves.

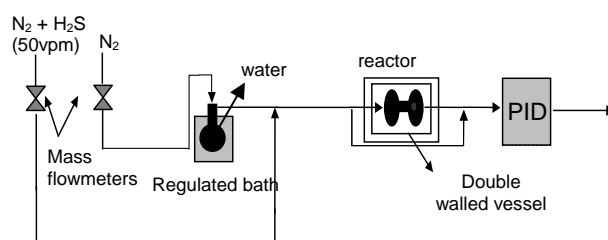


Figure 1 : Apparatus for measuring the H_2S sorption capacities of carbon fibres

The apparatus for the measurements of heat flows is illustrated on figure 2. The heat effects are detected by a calorimeter SETARAM C80. The heat flows recorded are plotted as a function of time by the software: setsoft 2000 from SETARAM. The integration of the calorimetric peaks, which can be done by the software, corresponds to the specific enthalpy of the reactions that occur in the cells.

The experimental protocol consists in introducing dry nitrogen in the cells of the calorimeter until the heat flow signal gets flat. Then half of the nitrogen flow is directed into a vessel filled with liquid water. The water partial pressure is fixed and controlled by the temperature of the water in the vessel. When the signal has been recovering the base line, the dry nitrogen flow is replaced by the H_2S flow. When the base line is recovered, only dry nitrogen is introduced in the cells.

All the thermal analyses are carried out under the following operating conditions: measured temperature 24.5°C, gas flow 3 L.h^{-1} , H_2S volumic fraction 50 vpm and relative humidity at 24.5°C 30%.

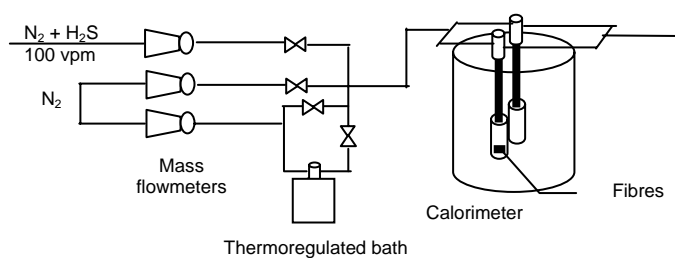
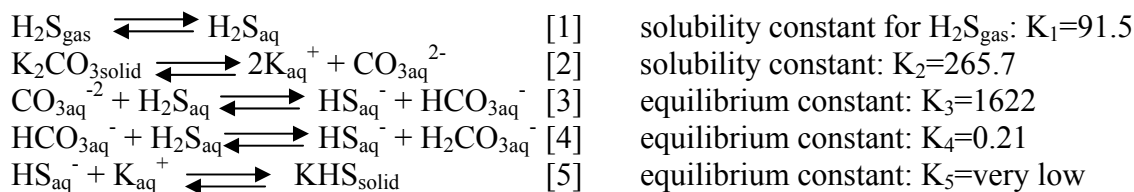


Figure 2 : Calorimetric apparatus

RESULTS AND DISCUSSION

1. H_2S fixation mechanism on the surface of impregnated carbon fibres.

H_2S fixation capacities of the carbon fibres are measured using the apparatus illustrated figure 1. Experiments evidenced that both impregnation treatment and that the presence of water vapour together with H_2S greatly enhance the H_2S fixation capacities of the fibres. After being in contact with H_2S , the impregnated fibre surface is analysed by X-rays diffraction: the sulphur matter loaded is KHS (potassium hydrogen sulphide). Considering these main results, a mechanism has been proposed to describe the fixation, in presence of water vapour, of H_2S gas on the surface of our modified activated fibres. The mechanism can be summarized as follows:



The large amount of water adsorbed forms a water layer ^[8,9] in which the impregnate and H_2S_g can dissolve and react together.

This mechanism highlights the essential role played by water. Without water vapour, no surface solution can be formed and no reaction can occur.

2. Results of the calorimetry study

For all the samples the curves obtained present the same shape (figure 3): they exhibit three peaks corresponding to the three steps already described: introduction of water vapour in the calorimeter cells, addition of H_2S_{gas} and finally introduction of dry nitrogen only.

The first peak is attributed to the adsorption of water and the dissolution of the impregnate.

The second peak is due to the H_2S fixation and the third peak to the desorption of water and the crystallisation of the remaining impregnate and KHS. This third peak will not be studied in this paper.

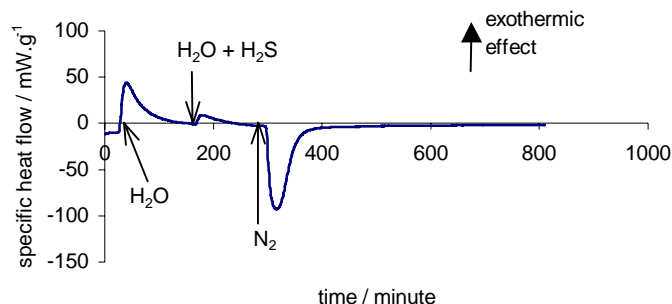


Figure 3 : Typical curve obtained following the experimental calorimetric protocol

A sample of virgin cloth has been introduced in the calorimeter cell. In such conditions, adsorption of water constituted the only contribution to the exothermal effect induced by the introduction of water vapour. The specific amount (per weigh of fibres) of water adsorbed, in the calorimeter operating conditions, has been determined by thermogravimetry, and the specific enthalpy of the reaction is deduced from the integration of the heat flow signal. These results leads to a molar enthalpy of -24 kJ.mol^{-1} (at 25°C) for the adsorption of water vapour. Water is linked to the surface of activated carbons by hydrogen bond established between the water molecules and the oxygenated surface groups or water molecules already adsorbed. The data found in the thermodynamic tables ^[10] for the hydrogen bonds energy vary between -20 and -25 kJ.mol^{-1} (at 25°C). So, the enthalpy measured is in fair agreement with the literature data.

To determine the dissolution enthalpy of K_2CO_3 in the water layer on activated fibres, calorimetric experiments on fibres impregnated in solution containing from 10 to 300 g.L^{-1} of KOH have been performed. The specific enthalpies corresponding to the first peak obtained for each impregnated fibre samples are plot as a function of the concentration of the impregnation solution (figure 4).

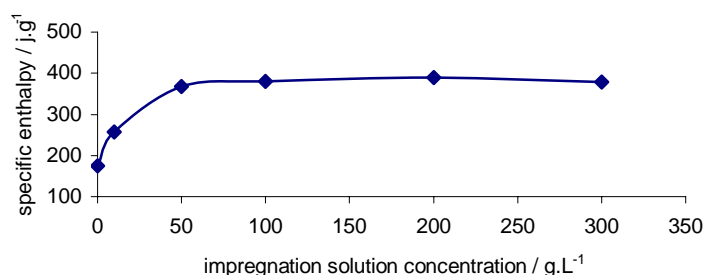


Figure 4 : Evolution of the water adsorption specific enthalpy with the concentration of the impregnation solution

The specific enthalpies increase until C_{KOH} reaches 100 g.L^{-1} . The amount of water adsorbed remains constant whatever the concentration of the impregnation solution. The evolution of the thermal effect induced by the introduction of water vapour in the calorimeter cells is due only to the dissolution of K_2CO_3 whose amount deposited increases with C_{KOH} . The solubility limit of K_2CO_3 is reached for KOH 100: so beyond $C_{\text{KOH}}=100 \text{ g.L}^{-1}$ the enthalpy does not increase any more but remains constant.

In thermodynamic tables ^[10], the value given for the enthalpy of dissolution of K₂CO₃ is equal at 25°C to -29 kJ.mol⁻¹. Experimentally, the same value has been obtained. This means that the aqueous surface solution present on the fibres surface behaves as a bulk solution.

All the experimental specific enthalpies of dissolutions for K₂CO₃ obtained are reported in table 1 and compared with the theoretical values. One can notice that theoretical and experimental values seem to be in good agreement.

	KOH 10	KOH 50	KOH 100	KOH 200
$\Delta H_{K_2CO_3 \text{ dissolution}} \text{ J.g}^{-1}$	20.2	53.7	57.7	61.6
$\Delta H_{\text{water adsorption}} \text{ J.g}^{-1}$	240	336	312	333
$\Delta H_{\text{theoretical}} \text{ J.g}^{-1}$	260	390	370	395
$\Delta H_{\text{experimental}} \text{ J.g}^{-1}$	258	361	380	390
variance	0.8%	7%	2.6%	1%

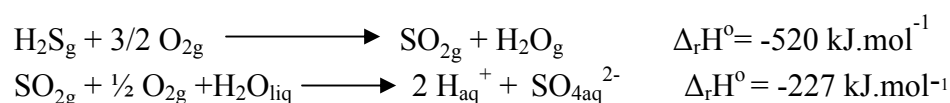
Table 1 : Experimental and theoretical enthalpies corresponding to the introduction of water vapour in the calorimeter cell containing impregnated cloth samples

The enthalpy corresponding to the second peak is greater for the virgin fibres than for the sample KOH 10. Actually, the amount of H₂S fixed, measured by integration of the breakthrough curves, is greater for the sample KOH 10 than for the virgin cloth. From this result one can conclude that the H₂S fixation mechanism is different according as the fibres are impregnated or not.

✧ *H₂S fixation on virgin fibres*

Without water vapour in the gas flow, the molar enthalpy for the fixation of H₂S is equal to: -30 kJ.mol⁻¹. This value corresponds to a physical adsorption. Without water vapour, the virgin fibres adsorb a small amount of H₂S: 3.2.10⁻⁴ mol.g⁻¹.

With water vapour in the gas flow (30% HR at 24.5°C), the amount of H₂S fixed does not exceed 2.7.10⁻⁵ mol.g⁻¹. One can conclude that H₂S and H₂O are adsorbed on the same sites. This result is not really surprising as they are both polar molecules which can be adsorbed only on polar oxygenated surface sites. As H₂O is introduced in the calorimeter cells before H₂S, the water molecules occupy the surface and leave no free site for H₂S. Nevertheless, some H₂S molecules are fixed on the surface of fibres because they are dissolved in the water layer formed on the fibre surface. The specific enthalpy for H₂S fixation on virgin fibres in presence of water vapour is quite huge: -833 kJ.mol⁻¹ (at 24.5°C). This value corresponds to enthalpies generally involved in chemisorption. The amount of H₂S molecules which dissolve in the surface solution exceed the solubility of this gas in these operating conditions (H₂S 50 vpm, 24.5°C) which is equal to 7.7.10⁻⁸ mol.g⁻¹. It can be deduced that H₂S dissolves in the surface solution and must be involved in some very exothermic reactions. These reactions could be oxidising reactions between H₂S and the surface oxygen ^[11]. As a reference the oxidation by gaseous oxygen yields two exothermic reactions:



The fixation mechanism of H₂S on virgin fibres in presence of water vapour could now be described as follows: formation of a water layer on the surface of the fibres, dissolution of

H_2S_{gas} in this layer, migration in solution towards the oxygenated surface groups and finally oxidation of H_2S molecules.

The analysis by ionic chromatography of a virgin fibres after being in contact with water vapour together with hydrogen sulphide evidenced the presence of sulphate ions on the surface of the fibres. This result confirms our hypothesis concerning the oxidation reactions that occur.

✧ H_2S fixation on impregnated fibres

The amount of K_2CO_3 deposited on the surface of the fibres and the H_2S fixation capacities of the impregnated fibres are reported in table 2 together with the theoretical and experimental variation of standard enthalpies corresponding to the H_2S fixation on the impregnated fibres.

	$K_2CO_3 / \text{mol.g}^{-1}$	Capacity / mol.g^{-1}	Experimental enthalpy / J.g^{-1}	Theoretical enthalpy / J.g^{-1}
Virgin cloth	0	$2.7.10^{-5}$	-20	
KOH 10	$0.65.10^{-4}$	12.10^{-4}	-12	-10.6
KOH 50	$17.8.10^{-4}$	$24.5.10^{-4}$	-22	-21.6

Table 2 : Data concerning H_2S fixation on virgin and impregnated fibres

The experimental specific enthalpies are obtained by integration of the calorimetric signals, the theoretical values are calculated. If n represents the amount of H_2S fixed, the theoretical specific enthalpy $\Delta_r H^{\circ}_{\text{th}}$ is given by:

$$\Delta_r H^{\circ}_{\text{th}} = \Delta_r H^{\circ}_{\text{dissolution}} \times n + \Delta_r H^{\circ}_{\text{reaction 4}} \times n/2 + \Delta_r H^{\circ}_{\text{reaction 5}} \times n/2$$

The reactions 4 and 5 corresponds respectively to the reactions between H_2S_{aq} and CO_3^{2-} and HCO_3^- .

$\Delta_r H^{\circ}_{\text{dissolution}} = -19.2 \text{ kJ.mol}^{-1}$, $\Delta_r H^{\circ}_{\text{reaction 4}} = 7.8 \text{ kJ.mol}^{-1}$ and $\Delta_r H^{\circ}_{\text{reaction 5}} = 13 \text{ kJ.mol}^{-1}$.

The experimental and theoretical data are in fair agreement.

When the concentration of the impregnation solution becomes greater than 50 g.L^{-1} , the surface solution becomes completely saturated and the H_2S_g is weakly dissolved onto the surface solution. For this reason, the H_2S fixation capacities start to decrease and the impregnate does not react entirely.

CONCLUSION

The study of the heat effects induced when the impregnated fibres are in contact with water vapour and then, water vapour and H_2S , allowed us to validate the H_2S fixation mechanism proposed. It also evidences oxidation reactions occurring when virgin fibres are in contact with the water vapour / H_2S gas flow.

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